REACTIVITIES OF DEWAR THIOPHENE CONTAINING TRIFLUOROMETHYL GROUPS

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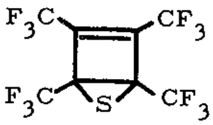
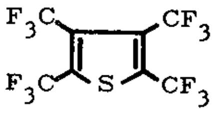
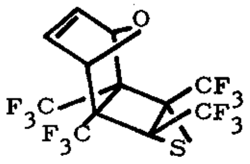
Tetrakis(trifluoromethyl)5-thia-bicyclo(2,1,0)pentene-2, Dewar thiophene (I), was prepared by photoreaction of tetrakis(trifluoromethyl)thiophene (II). Reactions of I were investigated. I changed to the dimer, dicyclobutenodithiane derivative, when dissolved in solvents such as DMSO or DMF. I isomerized to II at 180° in benzene. Trivalent phosphorus compounds, like triethyl phosphite, converted I to II, while pentavalent phosphorus compounds did not cause such isomerization. Adduct (III) was obtained through a Diels-Alder reaction between I and furan. III was desulfurated to 9-oxa-tricyclo(4,2,1,$0^{2,5}$)nona-3,7-diene derivative (IV) with triphenylphosphine at room temperature. When IV was irradiated in CH_3CN with a low-pressure mercury lamp at -10°, it gave oxa-homocubane derivative. Biradical mechanism (a) and the concerted one (b), which preceeds through tetrakis-(trifluoromethyl)cyclobutadiene and furan, have been proposed for this reaction. Since the reaction was not affected by 1,3-pentadiene, mechanism b seems slightly preferred. Diels-Alder reaction between I and tetramethylfuran gave an adduct the reaction of which with triphenylphosphine gave 1,6,7,8-tetramethyl-2,3,4,5-tetrakis(trifluoromethyl)9-oxa-tricyclo(4,2,1,$0^{2,5}$)nona-3,7-diene (VI).



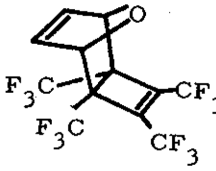
(I)



(II)



(III)



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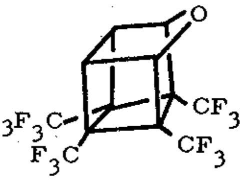
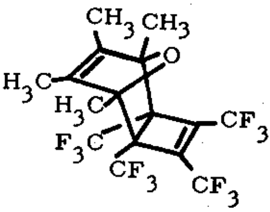
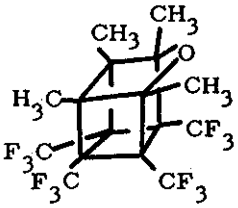


(V)



(VI)



(VII)